U.S. ENVIRONMENTAL PROTECTION AGENCY REGION 10

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1200 SIXTH AVENUE SEATTLE, WASHINGTON 98101

3 February, 1987

REPLY TO ATTN OF: M/S 329

MEMORANDUM:

SUBJECT: Analysis of Sediment Samples for Organotins, Auke Bay NOAA Laboratory

TO:

Michael Matta

Environmental Services Division

FROM:

Michael Watson Clary

Regional Toxicologist

On Monday, 2 February 1987, I telephoned Dr. Jeff Short, Chief Chemist with the NOAA laboratory at Auke Bay, Alaska (907) 789-6065. Please refer to my previous memo of 8 January, 1987, for details about the Auke Bay Laboratory's ability and willingness to analyze organotins for us.

I indicated to Dr. Short that we plan to sample about six sites at the two Marine Power facilities along the Duwamish River and in Lake Union, and that depending upon the results of our bioassays, we might wish to contract with their laboratory for organotin analysis of some of these samples. He indicated that they will need a minimum of about twenty grams of sample, and that samples which have been frozen in storage are fully acceptible. The samples should be sent frozen via air freight on Alaska Airlines, with prior notification of the Auke Bay Laboratory that they are to arrive on a given flight. He also indicated that there should be a "control" sample of background sediment submitted with the contaminated samples, and that the samples be coded in double blind fashion, so that the analyst will not know which samples are taken from contaminated areas.

Dr. Short also indicated that at the time we intend to send samples, final arrangements be made through the director of the Auke Bay Laboratory, Dr. George Snyder (telephone (907) 789-6000). Arrangements for paying the laboratory should also be made through Dr. Snyder. I am acquainted with him, and would be happy to be the contact, or to otherwise assist in any way I can. As I indicated in the previous memo, the cost will be \$25 per sample for a screening analysis which will tell us whether organically bound tin is present. A detailed analysis of specific organotin isomers will cost \$125 per sample.

The Auke Bay Laboratory is currently participating in a QA/QC program with twelve other labs in the U.S., which includes Battelle, the U.S. Navy, EPA Narragansett Labs, and so forth. The QA/QC effort is being coordinated by a NOAA facility at Monterrey, California.



I suggest we proceed in the following order: Each of the six sediments should be thoroughly mixed into a uniform slurry, each of which is then divided into three parts. One portion of the fresh slurry would then be subjected to bioassay. The other two portions would be retained frozen at the laboratory until the results of the bioassays are known. If the bioassays are significantly positive, then one portion would be sent to Auke Bay for preliminary analysis for total organotins, with instructions to them to retain enough sample to run detailed analysis later if desired. The remaining portion would then be analyzed at our laboratory for total metals other than tin.

We also discussed the possibility of detoxifying organotin in sediments. Organotins are quite sensitive to oxidation. Dr. Short indicated that in his opinion, it would not be difficult to simply detoxify the sediment effluent as the sediments themselves are removed. For brackish water sediments, this could be done by means of a simple flow-thru hydrolysis, generating free chlorine from seawater. The chlorine would act to oxidize the organotin to inorganic tin, which is toxicologically unremarkable. If we find that significant concentrations of toxic heavy metals other than tin are present, this method would of course become less worthwhile.

cc: William B. Schmidt

Paul Boys Monica Kirk Joe Cummins Bob Rieck M/S 329
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Michael Watson, Regional Toxicologist
Field Operations & Technical Support Branch

William B. Schmidt, Chief.
Field Operations and Technical Support Branch

On 7 January, 1987, I telephoned NOAA's Auke Bay Laboratory near Juneau, Alaska, and discussed the general issue of organotins in fish tissue and Bediment samples with Dr. Jeff Short. Telephone for Dr. Short is (907) 789-6065. Dr. Short and Dr. Frank Thrower of the Auke Bay lab have recently published a paper entitled "Accumulation of butyltins in muscle tissue of chinook salmon reared in sea pens treated with tri-n-butyltin". This paper was presented at the IEEE OCEANS '86 Conference in Washington, D.C., September 23-25, 1986. They are also preparing an upcoming paper on a screening method for organotins in fish muscle. Dr. Short related the following very interesting facts:

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- 1. The equipment and instrumentation necessary to accurately analyze organotins has cost the Auke Bay lab in the vicinity of 80-90 thousand dollars. This is because the lab uses a procedure which involves "mating" an atomic absorption (AA) detector with a gas chromatograph (GC). This union took them about eight months to successfully design and implement, because a certain amount of trial and error is required to compliment the undeniable skill required for the splicing. The concept for using the AA/GC combination was originated by Dr. Jim McGuire of Environment Canada, who pioneered Canada's efforts at analyzing organotins in marine samples. Dr. Short feels that the AA/GC method, despite its difficulties, is the best method by far, although one could also use a flame photometric detector with the GC instead of utilizing AA as the detector.
- 2. The best source of information regarding state-of-the-art extraction and analysis methods for organotins is Volume 4 of the Proceedings from the OCEANS '86 conference referenced above. I would recommend that the Region 10 laboratory acquire this volume for future references. Other pioneers in the field of organotin analysis in marine samples include: (a) Dr. Ed D. Goldberg, Scripps Institution of Oceanography, La Jolla, CA 92043, telephone ((619) 534-2407, and (b) Dr. Robert J. Huggett, Virginia Institute of Marine Science, College of William and Mary, Gloucester Pt., VA 23062, telephone (804) 642-7236.

3. The Auke Bay laboratory has recently sampled the common mussel, Mytilus edulus, from several locations along the Pacific coast, including several sites in Puget Sound. According to Dr. Short, mussels from Puget Sound (especially from the area around the Duwamish) contain significantly high levels of organotin. These samples are currently being analyzed, and the study is not yet completed. He will send me the data when they become available.

4. (saving the best news for last) The Auke Bay laboratory is interested in any contractual arrangements which EPA or others may wish to consider regarding analysis of marine samples for organotins. Two levels of analysis are available. For \$25 per sample, we would receive a screening analysis which will tell us whether or not organically bound tin is present, and a rough estimate of quantity. For about \$125 per sample, the lab will provide us with an AA/GC confirmation of each species of organotin present, with much greater quantitative accuracy. He suggests that samples be screened first with the cheaper method, and any positive samples then be analyzed in greater detail by the AA/GC method. I should also mention that NOAA is apparently cutting back funding for most of their laboratories. Facilities such as Auke Bay, Montlake and similar labs are thus very interested in soliciting outside funding via contractual arrangements.

I suggest that someone from our laboratory contact Dr. Short and explore mutual interests. If tributyl tin samples (Marine Power sediments, edible resource monitoring in Puget Sound, etc.) could be contracted out on a very limited initial basis, it would give us time to better explore the feasibility of gearing up internally for this complex analytical method over the long run.

cc: Mike Johnston
Bob Rieck
Roy Arp
Kathy Krueger
Dave Terpening
Steve Brown
Dave Tetta
Dave Heineck